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THERMODYNAMIC PROPERTIES OF GAS PHASE MOLECULAR IONS

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INTRODUCTION

Thermochemical properties of gas phase molecular negative ions have been determined from translational energy thresholds for endoergic reactions in which these ions are involved. Excitation functions for these reactions were obtained using a tandem mass spectrometer. Three types of reactions have been studied — charge transfer, particle transfer and collision-induced dissociation. Previously reported experiments conducted in our laboratory [1-8] have shown that reliable values of molecular electron affinities, bond dissociation energies and ionic heats of formation may be obtained from such measurements. New data relating to CO_3^- and O_3^- will be presented in the present paper, and results obtained for several other ions of interest will be reviewed.

EXPERIMENTAL

An in-line tandem mass spectrometer previously described [1-8] was utilized in this study. The projectile ion is formed in the electron-impact ion source of the first stage mass spectrometer which produces a mass and energy analyzed beam which is impacted upon the target gas in the collision chamber. The energy spread of the projectile ion beam entering the collision cell is about ± 0.3 eV (LAB) over the ion energy range, 0.3 to about 180 eV (LAB). Pulse counting techniques are used to measure the product ion current.

Projectile ions are produced by dissociative electron attachment using appropriate source molecules or by ion molecule reactions occurring in the primary ion source. For example, Br^- is produced by the direct electron impact process, $e + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{Br}^-$, while O_3^- is produced in a mixture of N_2O and O_3 by the sequence of reactions, $e + \text{N}_2\text{O} \rightarrow \text{O}^- + \text{N}_2$, and $\text{O}^- + \text{O}_3 \rightarrow \text{O} + \text{O}_3^-$. Ozone was produced in these studies by a Tesla coil discharge through O_2 , the excess O_2 being removed at -196°C [9]. Grease free, mercury free vacuum lines were employed and the fresh O_3 was directly introduced either into the ion source or into the collision chamber, as required.

Data Treatment and Corrections for Ion Energy
Distribution and Doppler Motion

The product ion intensity $I_s(E_{io})$ is converted to an observed apparent cross section [7]

$$\sigma_{\text{app}}^{\text{obs}}(E_{io}) = C[I_s(E_{io})/P_t]/I_p(E_{io}) \quad (1)$$

[†]On sabbatical leave from The Hebrew University of Jerusalem, 1976-77.

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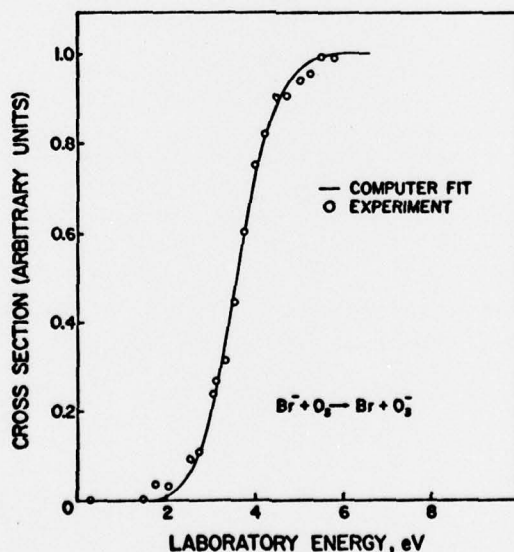
where $I_p(E_{10})$ is the primary ion intensity, E_{10} is the nominal reactant ion energy in the laboratory frame, P_t is the target gas pressure, and C is a conversion factor based on the intensity for the reaction O^-/NO_2 , for which the cross section is known.

Corrections for the ion energy distribution and Doppler motion of the neutral were applied as previously described [2,8]. A computer fitted excitation function based on these corrections, calculated using an assumed threshold function was compared in each case with the experimental data. The threshold behavior of the total cross section σ for collision-induced dissociation reactions is known from theoretical considerations [10]. The threshold functions for charge transfer and particle transfer have not been predicted theoretically. A model assuming a linear-plus-step function gave the best fit to most of the charge transfer data described here.

RESULTS AND DISCUSSION

Charge Transfer

Excitation functions were obtained for the charge transfer reactions of the projectile ions O^- , OH^- , S^- , SH^- , F^- , Cl^- , Br^- , I^- , NH^- , C_2H^- , NO_2^- and CO_3^- with O_3 . The experimental data points, as well as the computer fitted curve for the excitation function of the Br^-/O_3 reaction are shown in Fig. 1.



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Figure 1. Cross Section for the Reaction $Br^- + O_3 \rightarrow O_3^- + Br$ as a Function of Translational Energy. Points are experimental data. Solid line is the calculated "best-fit" excitation function.

The translational energy threshold of the linear-plus-step function threshold law employed for the computer fit (2.8 eV in the laboratory system), corresponds to an electron affinity of $EA(O_3) = 2.3$ eV. Other projectile ions gave similar results leading to an average value for the electron affinity of ozone of 2.28 ± 0.1 eV.

Particle Transfer

Considerable caution must be exercised when employing translational energy thresholds for particle transfer reactions in order to calculate their endoergicities. Many exoergic and thermoneutral reactions involving negative ions were observed to demonstrate translational energy thresholds due to the presence of energy barriers in their respective potential surfaces. Notable examples are the reactions, $O^-(H_2, H)OH^-$, $NH_2^-(H_2, NH_3)H^-$ and $D^-(H_2, HD)H^-$. The great advantage of beam experiments such as those reported here is the ability to determine excitation functions for both the forward and reverse steps of a particular particle transfer reaction. The non-existence of a translational energy threshold in the exoergic direction ensures that the translational energy threshold in the endoergic direction is equal to the endoergicity. This principle has been applied in studying the ozone system for which the following particle transfer reactions were investigated: $CO_3^-(O_2, CO_2)O_3^-$, $O_2^-(O_2, O)O_3^-$, $NO_2^-(O_2, NO)O_3^-$, $NO_3^-(O_2, NO_2)O_3^-$. The experimental data points and the corresponding computer fitted curve for the CO_3^-/O_2 reaction are shown in Fig. 2. The translational energy threshold yields a bond dissociation energy of $D(O_2 - O^-) = 1.6 \pm 0.1$.

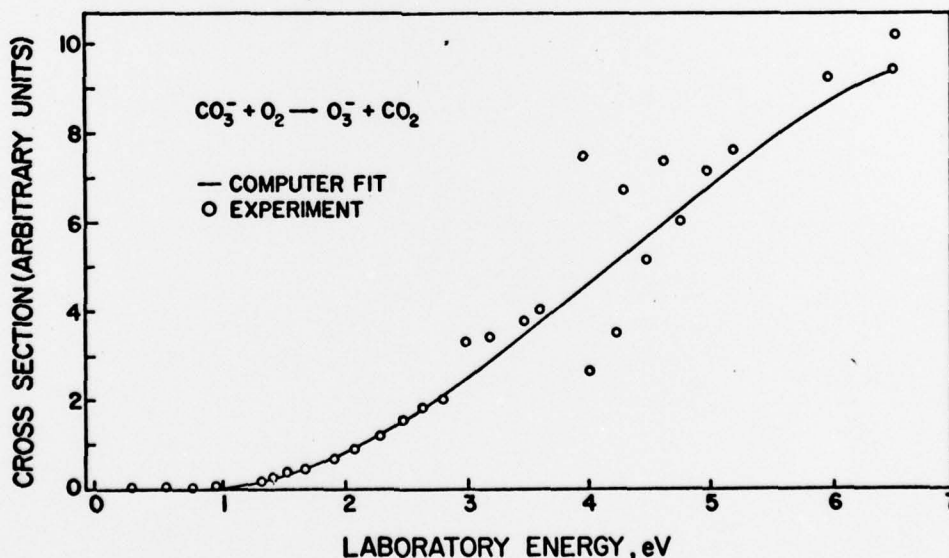


Figure 2. Cross Section for the Reaction $CO_3^- + O_2 \rightarrow O_3^- + CO_2$ as a Function of Translational Energy. Points are experimental data, solid line is the calculated "best-fit" excitation function.

Table I

BOND DISSOCIATION ENERGIES, HEATS OF FORMATION AND MOLECULAR ELECTRON AFFINITIES DERIVED FROM
TRANSLATIONAL ENERGY THRESHOLDS FOR ENDOERGIC NEGATIVE ION REACTIONS

Ion (XO_m^-)	$O^- - XO_{m-1}$ Bond Dissociation Energy (eV)	Heat of Formation		Electron Affinity of	
		XO_m^- (eV)	XO_m^- (eV)	XO_m^-	XO_m^-
NO^-	5.0 \pm 0.1 (CID)*	0.91 \pm 0.1 (CID)	0.02 \pm 0.1 (CID); 0.015 \pm 0.1 (CT)		
O_2^-	4.1 \pm 0.1 (CID)	-0.44 \pm 0.1 (CID)	0.44 \pm 0.1 (CID); 0.45 \pm 0.1 (CT)		
NO_2^-	4.0 \pm 0.1 (CID)	-2.0 \pm 0.1 (CID)	2.4 \pm 0.1 (CID); 2.28 \pm 0.1 (CT)		
N_2O^-	0.43 \pm 0.1 (CID)	0.62 \pm 0.1 (CID)	0.22 \pm 0.1 (CID)		
CO_3^-	2.0 \pm 0.1 (CID)	-4.98 \pm 0.1 (CID)	3.1 \pm 0.2 (CID)		
O_3^-	1.8 \pm 0.1 (PT)	-0.80 \pm 0.1 (CT) -0.74 \pm 0.1 (PT)	2.22 \pm 0.1 (PT); 2.28 \pm 0.1 (CT)		
$OH^-(H_2O)$ D($OH^- - H_2O$)	1.0 \pm 0.1 (CID)				

* CID - collision-induced dissociation; CT - charge transfer; PT - particle transfer

Collision-Induced Dissociation

Collisional dissociation thresholds have been measured to obtain the bond dissociation energies and heats of formation of molecular negative ions of O_2^- , NO^- , NO_2^- , N_2O^- , CO_3^- , O_3^- and NO_3^- . Rare gas atoms, diatomic and triatomic molecules served as collision reaction partners in these experiments. The corrected threshold data for CO_3^- yield a dissociation energy, $D(CO_2 - O^-) = 2.0 \pm 0.1$.

Data obtained for various negative ion species using the techniques described are summarized in Table I. These results will be compared with similar data obtained in other ion-beam, flowing afterglow, flow-drift, photodestruction and collisional ionization studies [11-16].

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Thermodynamic Properties of Gas Phase Molecules
Ions

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Introduction

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Thermodynamic properties of one phase calculated by using data from other phases have been used to determine the equilibrium constant for the reaction of the two phases. The equilibrium constant for the reaction of the two phases is calculated by using the data from the two phases. The equilibrium constant for the reaction of the two phases is calculated by using the data from the two phases.

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